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Annual fossil organic carbon delivery due to mechanical and chemical weathering of marly badlands areas

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Abstract

A key issue in the study of the carbon cycle is to well constrain stocks and fluxes in and between C-reservoirs. Amongst these, the role and importance of Fossil Organic Carbon (FOC) release by weathering of outcropping sedimentary rocks on continental surfaces is still debated and lacks measured constraint. Our work focuses on FOC fluxes due to chemical and mechanical weathering of marls in two experimental watersheds showing a typical badlands geomorphology (Draix watersheds, Laval and Moulin, Alpes de Haute Provence, France). Organic matter from bedrocks, soil litters and riverine

particles are characterized by Rock-Eval 6 pyrolysis. FOC fluxes due to mechanical weathering are then estimated by monitoring the annual particulate solid exports at the outlets of the watersheds (1985-2005 period). FOC fluxes from chemical weathering were calculated using Ca^{2+} concentrations in dissolved loads (year 2002) to assess the amount of FOC released by the dissolution of carbonate matrix. Results show that FOC delivery is mainly driven by mechanical weathering, with a yield ranging from 30 to 59 $\text{t km}^{-2} \text{ yr}^{-1}$ in Moulin (0.08 km^2) and Laval (0.86 km^2) catchments respectively (1985-2005 average). The release of FOC attributed to chemical weathering reach 2.2 to 4.2 t km^{-2} for the year 2002. These high FOC fluxes from badlands are similar to those observed in tectonically active mountain catchments. At a regional scale, badlands outcropping within the Durance watershed do not exceed 0.25 % in area of the Rhône catchment, but could annually deliver 12 000 t yr^{-1} of FOC. This flux could correspond to 27 % of the total Particulate Organic Carbon (POC) load exported by the Rhône River to the Mediterranean Sea. At a global scale, our findings suggest that erosion of badlands may contribute significantly to the transfer of FOC from continental surfaces to depositional environments.

Keywords: fossil organic matter, experimental watersheds, organic carbon fluxes, mechanical weathering, chemical weathering.

1. Introduction

Continental surfaces are composed of a combination of various sedimentary, metamorphic and plutonic rocks. Sedimentary rocks as shales, carbonates and

sandstones represent 65 % of the total continental surface (Amiotte-Suchet *et al.*, 2003). All of these rocks contain a variable Fossil Organic Carbon (FOC) content, generally comprised of between 0.01 to near 50.00 wt. % - with an average of 0.25 to 0.97 wt. % for carbonates and shales (Ronov and Yaroshevsky, 1976). At outcrop, FOC is generally considered fully mineralized and acts as a CO₂ source for the atmosphere (Berner, 1989; Berner and Canfield, 1989; Berner and Maasch, 1996). However, this assumption is in disagreement with numerous observations which suggest a natural resistance and FOC occurrence in various modern carbon reservoirs, including soils (Lichtfouse *et al.*, 1997a, 1997b; Di-Giovanni *et al.*, 1998a, 1999a, 1999b, 2000; Copard *et al.*, 2006; Graz *et al.*, 2010, 2011), rivers (Kao and Liu, 1996; Di-Giovanni *et al.*, 2000; Massiello *et al.*, 2001; Blair *et al.*, 2003, 2004; Raymond and Bauer, 2001, 2004; Copard *et al.*, 2006; Graz *et al.*, 2010, 2011; Hilton *et al.*, 2011) and recent sediments (Combaz, 1980; Tyson, 1995; Di-Giovanni *et al.*, 1997, 1998b, 1999b, 1999c, 2000; Eglinton *et al.*, 1997; Leithold *et al.*, 2001; Blair *et al.*, 2003; Dickens *et al.*, 2004a, 2004b; Wakeham *et al.*, 2004; Galy *et al.*, 2008a, 2008b), which indicates that the FOC is not completely oxidized. However, while the occurrence of FOC in various C-reservoirs is undisputable, the global flux of weathered FOC to the hydrosphere still remains unknown.

At a global scale, it is assumed that rivers carry between 0.04 to 0.08 Gt yr⁻¹ of particulate FOC to the world's oceans (Meybeck, 1993, 2005; Blair *et al.*, 2003). This input mainly originates from mechanical weathering of outcropping rocks or soils. Nevertheless, FOC release from the continents can not be directly related to the estimated FOC input to world's ocean, as an unknown fraction of FOC can be partially (Fredericks *et al.*, 1983; Lo and Cardott, 1995; Petsch *et al.*, 2000; Copard *et al.*, 2002)

or fully mineralised (Berner, 1989; Petsch *et al.*, 2000) during its storage and / or transfer within continental surfaces. Until now, we only know that the modelled FOC delivery due to chemical weathering (chemFOC) of shales and carbonates can reach between 0.04 to 0.09 Gt yr⁻¹ (Di-Giovanni *et al.*, 2002; Copard *et al.*, 2007). FOC flux originating from chemical weathering of sandstones is supposed negligible (Amiotte-Suchet *et al.*, 2003). For these latter fluxes, the lack of global estimate is related to the complex dependence on climatic and geological conditions. These chemFOC and FOC loads to oceans are estimated to be the same order of magnitude of the particulate Organic Carbon (OC) load delivered to world's oceans (between 0.09 and 0.43 Gt yr⁻¹, Ittekkot, 1988; Degens *et al.*, 1991; Berner, 1992; Meybeck, 1993; Ludwig *et al.*, 1996; Stallard, 1998; Schlunz and Schneider, 2000). Yet, the impact of FOC fluxes remains uncertain.

Here we quantify the flux of FOC due to mechanical and chemical weathering in two small experimental watersheds over annual to decadal timescales. The FOC is attributable to Jurassic marls weathering that contribute to 80 % of the suspended load of the “moyenne Durance”; one of the main tributaries of the Rhône River (Fournier, 2004). A classical geochemical analysis (Rock-Eval 6 pyrolysis) was used to characterize organic matter in studied samples (bedrocks, soil litters and riverine particles). FOC fluxes were estimated by monitoring the particulate (1985-2005 period) and dissolved (year 2002) exports at the outlet of the watersheds.

2. Material and methods

2.1. Study area

The study area corresponds to two experimental watersheds Laval (0.86 km²) and Moulin (0.08 km²) located near Digne (44° 08' 33''N, 06° 22' 05''E ; Alpes-de-Haute-Provence, France; Fig. 1) and overlying Callovo-Oxfordian marly limestones (Mathys *et al.*, 2003; Mathys, 2006). Such rocks are very sensitive to weathering and develop typical badlands morphology with V-shapes gullies, producing very high sediment loads (>10 g/L) during floods (Mathys *et al.*, 2003). These two experimental watersheds deliver a sediment yield of 5 700 t km⁻² yr⁻¹ in Moulin and 11 200 t km⁻² yr⁻¹ in Laval (Mathys *et al.*, 2003) comparable to other badlands located around the Mediterranean Sea (Nadal Romero *et al.*, 2011). These watersheds present different vegetal cover densities: Laval (32 %), and Moulin (46 %) (Mathys *et al.*, 2003).

2.2. Previous results

72 watershed samples (bedrock: 5 samples; soils: 15 samples; regolith profiles (bedrocks to soils): 44 samples; riverine particles: 8 samples) were previously examined in order to distinguish fossil and recent organic matter (Copard *et al.*, 2006; Graz *et al.*, 2011). We used complementary techniques: optical (palynofacies methods), geochemical (Rock-Eval 6 pyrolysis, C/N ratio), molecular (gas chromatography/mass spectrometry) and isotopic (stable C isotopic composition) analyses. These investigations were completed by quantitative palynofacies analysis performed on 82 samples from Laval watershed (bedrock, regolith profiles, soils: 72 samples; riverine particles: 10 samples, Graz *et al.*, 2010). Fossil and recent organic markers were identified and tracked through the different organic carbon reservoirs. The results permit us to (i) quantify bedrock organic content varying between 0.10 (limestones) and 0.50 – 0.70 wt. % (marls) - such values are of the same order as the average value (0.50

wt. %) obtained by Artru (1972) on 6 000 callovo-oxfordian marls samples; (ii) distinguish recent and fossil organic matter and highlight the contribution of Fossil Organic Matter (FOM containing FOC), which can be found in all the studied organic carbon reservoirs. FOM contribution to total organic matter varies from 5.5 to 70.0 % in soils, 20.0 to 95.0 % in regolith profiles and 47.0 to 91.0 % in riverine particles (Graz *et al.*, 2010, 2011).

2.3. Strategy, organic matter characterization and samples design

Compilation of the data (Copard *et al.*, 2006; Graz *et al.*, 2010, 2011, see section 2.2.) indicates that FOM contribution was only quantified for 18 published riverine samples between years 2002 and 2008. However, this small number of samples is not sufficient to estimate annual FOM (and thus FOC) fluxes at the watersheds outlets. In order to address this issue, a calibration of Rock-Eval 6 parameters using previous quantitative palynofacies results was performed (bedrock, regolith profiles, soils and riverine particles, Graz *et al.*, 2010). The obtained HI / FOM relation was applied to 60 other riverine samples in order to directly distinguish fossil and recent organic carbon (see section 3.1.). These samples were collected by using automatic sampling between 1999 and 2008 at Laval (30 suspended load / 6 bed load) and Moulin (24 suspended load) outlets.

Rock-Eval 6 pyrolysis (RE6, Vinci Technologies®), a method previously developed for petroleum purposes and the analysis of sedimentary rocks, is now successfully applied for recent material (soils and recent sediments, Di-Giovanni *et al.*, 1997, 1998b; Noël *et al.*, 2001; Disnar *et al.*, 2003; Copard *et al.*, 2006; Sebag *et al.*, 2006). The protocol consists of two successive stages performed under a temperature program of 30 °C min⁻¹

¹. The former consists of pyrolysis of 100 mg of crushed sample in an oven. Hydrocarbon and oxygenated products released during a temperature increase from 200 to 650 °C are removed via a N₂ flow and quantified with flame ionization and infrared detectors respectively. The second stage consists of oxidation in an oven of the carbonaceous residue subjected to a temperature increase from 400 to 750°C (Lafargue *et al.*, 1998). Analysis of the pyrolysis signals provides some classical parameters such as Hydrogen Index (HI, in mg HC g⁻¹ TOC), which can be defined as an indicator of the hydrogen richness of the organic matter. The Organic Carbon content (OC) is given by the Total Organic Carbon (TOC, expressed in wt. %), equal to the sum of pyrolysed OC and residual OC provided by the oxidation stage.

A first study dealing with the development of quantitative palynofacies was already published (Graz *et al.*, 2010). This method allowed us to determine organic particles mass concentrations and to discriminate Recent Organic Matter (ROM) from Fossil Organic Matter (FOM containing FOC) in 82 samples from Laval watershed (bedrock, regolith profiles, soils: 72 samples; riverine particles: 10 samples). Rock-Eval pyrolysis was also performed for all these samples. HI values (11 to 180 mg HC g⁻¹ TOC) and the relative proportion of ROM (0.0 to 88.0 %) were used to calibrate Rock Eval parameters in order to obtain fossil and recent carbon proportions in all studied samples (see 3.1.). Results are listed online in supplementary material.

2.4. Calculation of FOC fluxes released by bedrocks mechanical (mecFOC) and chemical weathering (chemFOC)

Draix riverine particles are the product of mechanical weathering of the bedrock (Di-

Giovanni *et al.*, 2000; Copard *et al.*, 2006). mecFOC can be calculated by considering FOC content of bedrocks and their annual fluxes. Such calculations were possible since the studied watersheds were previously equipped by Cemagref in order to estimate both the water discharge and fine and coarse solid transports (see Richard and Mathys, 1999; Mathys *et al.*, 2003; Klotz *et al.*, 2005; Mathys, 2006; for further details). At the outlet of Laval and Moulin catchments, a gauging station, with a calibrated flume is equipped with a series of recorders (e.g. floating device, ultrasonic sensor, radar sensor). Upstream of this flume a sediment trap retains the coarse material. This method gives a total amount of bed load conveyed by the streams. In the gauging flume, an automatic sampler takes samples during floods with a program referring to both the level of water and the time lag between two samples, giving a discontinuous estimation of fine solid transport during a flood. Since 1995, prototypes of optical fiber sensors were installed and provide measures sediment concentration of the flow using back scattering properties of the mixture. As a result, combined sediment concentration and discharge measurements allow one to calculate the suspended sediment yield for flood events and on annual timescales.

The dissolution of rocks that contain carbonates produces dissolved carbonates and an insoluble residue that can contain organic carbon if the parent rocks contained organic matter. If the yield of dissolved carbonates and the initial carbonates content of the parent rocks are known, then the yield of the insoluble residue can be calculated (Di-Giovanni *et al.*, 2002). Furthermore, if the initial FOC content in the parent rock is known, then the amount of FOC yielded from the dissolution of the carbonate matrix can be estimated. Calculations were only possible for the year 2002. Indeed, Cras (2005) carried out a multi-scale hydrochemical investigation over one year in Laval and

Moulin catchments, including both high flow and low flow periods. Automatic water samplers were used to collect water during the high flows periods whereas low flow waters were hand sampled. According to the flood events, the sampling frequency could reach 5 min. During low flow periods, a weekly sampling was carried out. Mean concentration estimates were calculated from 163 and 208 samples in Laval (including 6 flood events) and in Moulin (including 6 flood events) respectively. Cras *et al* (2007) showed that rainfall did not contain significant amount of Ca^{2+} . Accordingly, we can consider that Ca^{2+} measured at the outlet of the watersheds mainly originated from bedrock chemical weathering.

3. Results

3.1. Rock-Eval 6 pyrolysis parameters calibration

There is a significant correlation between previously determined proportions of ROM (Recent Organic Matter - by opposition to FOM - Graz *et al.*, 2010) and HI values from Rock-Eval pyrolysis ($R^2 = 0.93$, Fig. 2) for 82 samples from Laval watershed (bedrock, regolith, soil and riverine particles, see online supplementary material for more details). Accordingly, a relationship between HI values and ROM % can be defined and lead to the quantification of FOM % ($\text{FOM \%} = 100 - \text{ROM \%}$) in riverine suspended sediments following the equation (Eq.1):

$$(\text{Eq 1}) \text{ HI (mg HC.g}^{-1} \text{ TOC)} = 1.7927 \times \text{ROM (\%)} + 10.292$$

Uncertainties on HI values (5%) are widely lower than those on palynofacies results (15 %, Graz *et al.*, 2010). Uncertainties on calculated FOM % values are then close to 15 %.

3.2. FOC content of riverine particles

Riverine particles present low TOC and HI values (0.46 to 0.65 % and 19 to 72 mg HC g⁻¹ TOC respectively, Tables 1 and 2) that are similar, but slightly higher, to those observed in bedrocks samples (Graz *et al.*, 2010).

The observed relationship between HI values and ROM % (Fig. 2) permits to estimate FOC and Recent Organic Carbon (ROC) contents (wt. %) ($\text{FOC} = \text{TOC} \times \text{FOM} \%$; and $\text{ROC} = \text{TOC} \times \text{ROM} \%$) in all studied riverine samples (Laval, Table 1 and Moulin, Table 2). FOC content appears constant in all studied samples and close to 0.5 wt. % (+/- 0.07, 60 samples). This is in agreement with previous results (18 samples) showing that riverine particles of these watersheds are the direct product of bedrocks mechanical weathering (Di-Giovanni *et al.*, 2000; Copard *et al.*, 2006; Graz *et al.*, 2010).

The higher ROC values (from 0.1 to 0.2 wt. %) are obtained for Moulin suspended load samples, which also exhibits a large area of vegetation cover (46 %, Mathys *et al.*, 2003). The lower ones (< 0.1 %) are obtained for Laval suspended load samples, where the vegetal cover area is somewhat lower (32 %, Mathys *et al.*, 2003).

3.3. FOC fluxes released by bedrocks mechanical weathering

Measurements of solid export values at the outlets (Klotz *et al.*, 2005; Mathys, 2006) are highly variable from one year to another but also from one basin to another (Table 3). The export loads at Laval outlet range from 4352 - 21148 t km⁻² yr⁻¹ compared to

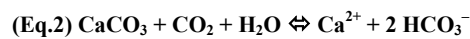
1350 - 9990 t km⁻² yr⁻¹ at Moulin outlet. With respect to the spatial scale (area) and badlands context, these magnitudes are comparable to those observed for numerous badlands area, located around the Mediterranean Sea (Nadal-Romeo *et al.*, 2011).

Considering that the FOC content of these loads is close to 0.5 wt. % (Tables 1 and 2, see also section 3.2.), mecFOC can be calculated. Obtained values range between 22 and 106 t km⁻² yr⁻¹ for Laval, and between 7 and 50 t km⁻² yr⁻¹ for Moulin (Table 3). The inter-annual FOC fluxes average 59 and 30 t km⁻² yr⁻¹ respectively.

3.4. FOC fluxes release by bedrocks chemical weathering

Exported total dissolved load were 340 and 570 t km⁻² for the year 2002 respectively for Laval and Moulin (Table 4; Cras, 2005). Total Dissolved Solid (TDS) concentrations reached an average of 13.4 and 11.7 mmol l⁻¹ respectively in watershed waters and Ca²⁺ concentrations reached 2.5 and 2.4 mmol l⁻¹ (Table 4).

Ca²⁺ concentrations measured at the outlets of watersheds originate from the bedrocks carbonate dissolution as rainwater does not contain Ca²⁺ (Cras *et al.*, 2007). This dissolution is illustrated by the following equation (Eq.2):



On this basis, the estimation of the chemical weathered bedrock mass (t km⁻² yr⁻¹) can be obtained following three steps (Eqs.3, 4 and 5).

$$\text{(Eq.3) Annual Ca}^{2+} \text{ fluxes (t km}^{-2} \text{ yr}^{-1}) = \mathbf{M} \times \mathbf{Ca}^{2+} \text{ \%}$$

Where M is dissolved load exported from the watersheds in 2002 (Table 4) and Ca% is the Ca^{2+} content in TDS from riverine waters (18.7 and 20.5 for Laval and Moulin respectively).

$$\text{(Eq.4) Annual mass of dissolved CaCO}_3 \text{ (t km}^{-2} \text{ yr}^{-1}\text{)} = \text{annual Ca}^{2+} \text{ fluxes} \times 2.5$$

Where 2.5 correspond to the molar mass of Ca reported to the molar mass of CaCO_3 (100 / 40).

$$\text{(Eq.5)}$$

$$\text{Mass of altered bedrock (t km}^{-2} \text{ yr}^{-1}\text{)} = \text{Annual mass of dissolved CaCO}_3 \times (100 / \text{Tc})$$

Where Tc is the CaCO_3 content of watersheds bedrocks (i.e. 35 %, Simmonet *et al.*, 1995).

Considering the bedrocks average TOC (0.50 wt. %, Artru, 1972; Graz *et al.*, 2010) and the annual mass of altered bedrocks, chemFOC (t km⁻² yr⁻¹) can be calculated as follows:

$$\text{(Eq.6) chemFOC (t km}^{-2} \text{ yr}^{-1}\text{)} = \text{Mass of altered bedrock (t km}^{-2} \text{ yr}^{-1}\text{)} \times \text{bedrock TOC (0.50 wt. \%)}$$

FOC fluxes inherited from chemical weathering of bedrocks (chemFOC) can be further mineralized, dissolved or stored as a insoluble residue. They reach 2.2 and 4.2 t km⁻² yr⁻¹ for Laval and Moulin watersheds, respectively.

4. Discussion

4.1. FOC fluxes

For these watersheds, FOC input in continental surfaces is mainly controlled by mechanical weathering (average mecFOC from 30 to 59 t km⁻² yr⁻¹, Table 3) while chemFOC fluxes, inherited from chemical weathering of bedrocks and considered as an insoluble residue, are much lower (from 2 to 4 t km⁻² yr⁻¹, year 2002). This strong difference between mechanical and chemical FOC estimates is not a surprise with respect to the geomorphological context (badlands) of these watersheds, marked by predominant gully erosion.

However in our study, the estimated chemFOC fluxes in Moulin catchment (4.2 t km⁻² yr⁻¹) are twice that of Laval catchment (2.2 t km⁻² yr⁻¹). This suggests that chemical weathering is more efficient within the former catchment. One of the possible causes to explain this variation would be the higher extent of forest area in Moulin (46 %) than in Laval (32 %, Mathys *et al.*, 2003). Indeed, it is well known that a large area of forest cover leads to a decrease in the runoff intensity (e.g. Campy and Macaire, 2003). Such context would favor the storage of FOC as an insoluble residue; which can be stored and subsequently mineralized in regoliths or soils or even exported if a future mechanical weathering occurs prior to its mineralization. mecFOC fluxes are globally twice higher for Laval (59 t km⁻² yr⁻¹) than for Moulin (30 t km⁻² yr⁻¹) catchments. Again, a possible cause for this variation is the lower forest cover in Laval catchment (32%). This could also be exacerbated by the higher mean slope values observed for Laval (58%, Mathys *et al.*, 2003), which should inhibit the development of forest cover and promote the mechanical weathering via an efficient runoff and erosion processes (Dietrich *et al.*, 2003).

mecFOC yields from the studied catchments are of the same order of magnitude as FOC yields previously reported in suspended sediments from tectonically active mountain catchments in USA/California ($9 \text{ t km}^{-2} \text{ yr}^{-1}$ Eel river, Blair *et al.*, 2003; Leithold *et al.*, 2006; $11 \text{ t km}^{-2} \text{ yr}^{-1}$ Santa Clara river, Blair *et al.*, 2003; Komada *et al.*, 2004), New Zealand ($14 \text{ t km}^{-2} \text{ yr}^{-1}$ Southern Alpines rivers, Hilton *et al.*, 2008; $29 \text{ t km}^{-2} \text{ yr}^{-1}$ Waipaoa river, Gomez *et al.*, 2003; Leithold *et al.*, 2006) and Taiwan ($19 \text{ t km}^{-2} \text{ yr}^{-1}$, Lanyang Hsi, Kao and Liu, 1996, from 12 to $246 \text{ t km}^{-2} \text{ yr}^{-1}$, Hilton *et al.*, 2011). Our results suggest that high mecFOC transfers in particulate load are not restricted to tectonically active mountains belts. Steep terrain and weak sedimentary rocks give rise to the high calculated yields herein. As such, the delivery of FOC to depositional setting may be more widespread than previously thought (e.g. Blair *et al.*, 2003; Hilton *et al.*, 2011).

4.2. Fate of FOC in continental surfaces

The riverine particles at outlets of these watersheds reach the Rhône delta in less than five days (IRS, 2001). This suggests a very short transit time and little storage of FOC within the Durance and the Rhone catchments, which can be considered as a conduit for transporting FOC to the Mediterranean Sea. Consequently FOC delivered by mechanical weathering could significantly contribute to Rhône rivers organic content. Considering that, (i) at a regional scale (Durance catchment), watershed badlands outcrops area, where erosion of FOC is likely, reach 233 km^2 (Brochot, 1999; Rey *et al.*, 2007), (ii) all of these badlands present a similar erosion rate (Saignon and Savournon watersheds, Olivry and Hoorelbeck, 1990; Rey, 2002; Ray *et al.*, 2002) which are also comparable to other badlands area located around the Mediterranean sea

(Nadal Romero *et al.*, 2011) and (iii) the average mecFOC we obtained is $52 \text{ t km}^{-2} \text{ yr}^{-1}$, such formations covering at best 0.25 % of the Rhône watershed (97800 km^2), could likely deliver $12\,000 \text{ t yr}^{-1}$ of FOC to the Mediterranean Sea. This flux could correspond to 27 % of the total particulate organic carbon annually delivered by the Rhône river ($44\,080 \text{ t yr}^{-1}$, Ludwig *et al.*, 1996). This C-kerogen (FOC) has been recorded in marine sediments of Gulf of Lion (Gadel and Ragot, 1973) that are likely fed by Rhone sediments (Cauwet *et al.*, 1990). Such FOC reburial in marine sediments suggests the balance between OC burial and FOC oxidation maintaining atmospheric O_2 constant (Bernier, 1989; Bernier and Canfield, 1989) is not completed (Hilton *et al.*, 2011). This also means that O and C cycles should be revisited in the light of this FOC route for which a significant part, strongly controlled by the chemical and physical properties of kerogen (Copard *et al.*, 2007; Galy *et al.*, 2008b), may be reburied (e.g. Hilton *et al.*, 2011).

FOC delivered by chemical dissolution of bedrocks with carbonate matrix (e.g. marls) can be mineralized, dissolved or stored in regoliths and soils. Its resident time in soils could be close to 10^4 years (Keller and Bacon, 1998; Petsch *et al.*, 2000). However this duration is purely theoretic and should be considered with care as the mineralization rate firstly depends on chemical and physical properties of FOC. On the whole, the recalcitrant character of FOC increases with the richness of C content associated to H depleted content of kerogen (Joseph and Oberlin, 1983). This implies that higher burial temperature of kerogen produces material more recalcitrant to chemical weathering as oxidation, hydrolysis or biodegradation. In other terms, a mature kerogen reaching the gas window (close to the methagenesis, Durand, 1980) as metha-anthracites or the ultimate C-member, graphite, could be persistent over a long period in continental

surfaces and can be exported to oceans (Galy *et al.*, 2008b; Bouchez *et al.*, 2010). For some lower degree of thermal evolution, kerogen resistance toward weathering is governed by its chemical composition inherited from the biological precursors and previous processes experienced before burial. Accordingly, a kerogen showing a ligno-cellulosic origin (type III in a Van Krevelen diagram) with a high proportion of aromatic sheets, exhibits a higher resistance toward weathering than a kerogen consisting in bacterial and/or algale origin (type I and II in a Van Krevelen diagram) with rather a higher proportion of aliphatic compounds likely to be preferentially attacked by oxidation (Copard, 2002 and references therein). However analysis of soil OM modulates this simplistic postulate where some rich-aliphatic compounds appear to be highly resistant towards soil processes (e.g. Lichtfouse *et al.*, 1998). As some field examples, mineralization rates of FOC of outcropping humic coals ranged from different ranks (from low to high volatile bituminous coals) are comprised between 20 to 45% (Fredericks *et al.*, 1983; Lo and Cardott, 1995; Copard *et al.*, 2002) while C-kerogen of outcropping black shales (phytoplanktonic-derived origin) present a complete mineralization (Petsch *et al.*, 2000). For the FOM disseminated in outcropping marls of the Draix experimental catchments, FOM is dominantly a type III kerogen (Graz *et al.*, 2010, 2011). During Jurassic, these marls were deposited in marine environments where a mixture between marine and continental organic matter classically occurs (Artru, 1972). Without any further alterations, and regarding the maturity level reached by the kerogen disseminated in these rocks during burial (attested by a low Tmax values, <410°C, from the RE6 pyrolysis, Copard *et al.*, 2006; Graz *et al.*, 2011), this kerogen would have exhibited some HI values higher than 400 mg HC g⁻¹ TOC (Espitalié *et al.*, 1985). However, for the examined rocks, HI values

never exceed 180 mg HC g⁻¹ TOC and highlight that this kerogen is already weathered. This means that the kerogen has already lost a significant (but unknown) amount of labile FOC prior analyses, during a chemical weathering as the weathering front can dip several meters from the soil surface (e.g. Petsch *et al.*, 2000). This kerogen, or more precisely this recalcitrant “residual kerogen”, is thus resistant against further weathering. This could explain why the observed mineralization rates of FOC along some previously studied regolith profiles in these catchments never exceed 30 % (Graz *et al.*, 2011). As a consequence, a significant part of FOC released by chemical weathering of bedrocks can be stored in regoliths.

Unfortunately, constraint on the chemical composition of kerogen is not sufficient to predict its persistence in continental surfaces. External factors of climate, geological context and more recently of Human disturbances (e.g. Land Use Change on forest cover) in continental surfaces advance or mitigate the mineralization rate. As an example the aggressiveness of climate, both temperatures than precipitations amount as seen in tropical climate, would improve the mineralization rate of any OM including kerogen with a higher biodegradation or oxidation processes. If this FOC escapes from such processes, soil can be further eroded and deliver its FOC to rivers as part of the particulate load.

5. Conclusions

This study proposes a first assessment of FOC fluxes release by mechanical and chemical weathering of marls in badlands. With values ranging from 30 to 59 t km⁻² yr⁻¹, fluxes due to mechanical weathering are predominant and are the same order of

magnitude than those previously estimated from tectonically active mountain catchments (9 to 246 t km⁻² yr⁻¹). These significant values are not surprising in badlands due to weak substrate and high local slope in gully valleys which drive high physical erosion rates. At the scale of the lower course of the Rhone river, we assume that such geological formations could annually export 12 000 t of FOC into the Mediterranean Sea. At global scale, rivers draining such badlands, whose lithology is mainly composed of marls and clayed rocks (Nadal Romero *et al.*, 2011) rich in organic carbon, could be also a significant source of FOC in continental surfaces. This FOC can be conveyed downstream of the river with the clastic load to ocean sediments with implications for the global C and O biogeochemical cycles (Berner 1989; Blair *et al.*, 2003).

FOC fluxes caused by the chemical dissolution of the bedrock during weathering are lower and reach respectively 2.2 and 4.2 t km⁻² yr⁻¹ for Laval and Moulin watersheds. Despite a high resistance of this FOC against weathering, this could promote storage as insoluble residues (soils, regoliths), and a part of this carbon can either be mineralized or dissolved.

At global scale, the fate of FOC depends on several parameters as the physical and chemical properties of FOC (origin, temperature recorded during OM burial), the duration of exposure to weathering, but also on the nature and hence the aggressiveness of the weathering processes (e.g. hydrolysis, bacterial activity).

Our results confirm that the release of FOC by mechanical and chemical weathering of sedimentary rocks does not simply act as a source of C to the atmosphere, but can also supply other carbon reservoirs (soils, riverine particles, sediments). Fossil contribution should be taken into account by other studies based on organic matter data and the role of FOC in the carbon cycle has to be revisited.

Acknowledgements

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Figures and Tables captions

Fig. 1. Geographical location of Draix experimental watersheds (after Lopez Saez *et al.*, 2011).

Fig. 2. HI (mg HC g⁻¹ TOC) vs. Recent Organic Matter proportions (ROM %) for 82 samples (Laval watershed). Uncertainties on HI values: 5 %; uncertainties on ROM proportions: 15 %.

Table 1. Rock-Eval 6 parameters (TOC and HI), ROM / FOM proportions, and ROC / FOC contents for 36 Laval riverine particles.(Suspended load (SL) and bed load (BL)).

Table 2. Rock-Eval 6 parameters (TOC and HI), ROM / FOM proportions, and ROC / FOC contents for 24 Moulin riverine particles.(Suspended load (SL) and bed load (BL)).

Table 3. Sediment and FOC (mecFOC) yields for the Laval and Moulin watersheds.

Table 4. Dissolved load yield for Laval and Moulin catchments, Ca²⁺ and Total Dissolved Solid (TDS) concentrations in watershed waters (year 2002; after Cras, 2005).

table 1

Samples	TOC %	HI (mg HC g ⁻¹ TOC)	ROM % (% 15%)	FOM % (% 15%)	FOC wt. % (% 15%)	ROC wt. % (% 15%)
Laval SL						
03/05/2002a	0.55	25	8.2	91.8	0.5	<0.1
Laval SL						
03/05/2003b	0.51	33	12.7	87.3	0.4	0.1
Laval SL						
13/05/2002	0.55	36	14.3	85.7	0.5	0.1
Laval SL						
24/05/2002	0.51	27	9.3	90.7	0.5	<0.1
Laval SL						
26/08/2002	0.53	34	13.2	86.8	0.5	0.1
Laval SL						
02/09/2002	0.52	27	9.3	90.7	0.5	<0.1
Laval SL						
05/09/2002	0.50	30	11.0	89.0	0.4	0.1
Laval SL						
23/10/2002	0.55	24	7.6	92.4	0.5	<0.1
Laval SL						
06/07/2006	0.47	21	6.0	94.0	0.4	<0.1
Laval SL						
07/07/2006	0.56	25	8.2	91.8	0.5	<0.1
Laval SL						
12/07/2006b	0.65	23	7.1	92.9	0.6	<0.1
Laval SL						
12/07/2006a	0.56	20	5.4	94.6	0.5	<0.1
Laval SL						
18/07/2006b	0.46	19	4.9	95.1	0.4	<0.1
Laval SL						
18/07/2006a	0.51	20	5.4	94.6	0.5	<0.1
Laval SL						
08/09/2006	0.62	19	4.9	95.1	0.6	<0.1
Laval SL						
15/09/2006	0.52	25	8.2	91.8	0.5	<0.1
Laval SL						
25/09/2006	0.58	19	4.9	95.1	0.6	<0.1
Laval SL						
20/10/2006a	0.54	26	8.8	91.2	0.5	<0.1
Laval SL						
20/10/2006b	0.53	28	9.9	90.1	0.5	0.1
Laval SL						
20/10/2006c	0.52	29	10.4	89.6	0.5	0.1
Laval SL						
07/12/2006a	0.52	25	8.2	91.8	0.5	<0.1
Laval SL						
07/12/2006b	0.52	23	7.1	92.9	0.5	<0.1
Laval SL						
04/06/2007	0.54	33	12.7	87.3	0.5	0.1
Laval SL						
05/06/2007b	0.60	32	12.1	87.9	0.5	0.1
Laval SL						
05/06/2007a	0.62	24	7.6	92.4	0.6	<0.1
Laval SL						
16/09/2007	0.53	21	6.0	94.0	0.5	<0.1
Laval SL						
22/11/2007	0.48	19	4.9	95.1	0.5	<0.1
Laval SL						
11/01/2008a	0.61	23	7.1	92.9	0.6	<0.1
Laval SL						
11/01/2008b	0.55	24	7.6	92.4	0.5	<0.1
Laval SL						
11/01/2008c	0.53	28	9.9	90.1	0.5	0.1
Laval BL						
24/09/1999a	0.49	14	2.1	97.9	0.5	<0.1
Laval BL						
24/09/1999b	0.46	11	0.4	99.6	0.5	<0.1
Laval BL						
24/09/1999c	0.59	29	10.4	89.6	0.5	0.1
Laval BL						
	0.42	14	2.1	97.9	0.4	<0.1

20/11/2006a						
Laval BL						
20/11/2006b	0.45	18	4.3	95.7	0.4	<0.1
Laval BL						
20/11/2006c	0.60	22	6.5	93.5	0.6	<0.1
Average	0.53	24	7.7	92.3	0.5	<0.1

table 2

Samples	TOC %	HI (mg HC g ⁻¹ TOC)	ROM % (%15 %)	FOC % (%15 %)	FOC wt. % (%15 %)	ROC wt. % (%15 %)
Moulin SL						
13/05/2002	0.60	72	34.4	65.6	0.4	0.2
Moulin SL						
03/05/2002	0.56	30	11.0	89.0	0.5	0.1
Moulin SL						
05/08/2002	0.53	28	9.9	90.1	0.5	0.1
Moulin SL						
27/08/2002a	0.54	43	18.2	81.8	0.4	0.1
Moulin SL						
27/08/2002b	0.51	29	10.4	89.6	0.5	0.1
Moulin SL						
02/09/2002	0.56	45	19.4	80.6	0.5	0.1
Moulin SL						
05/09/2002	0.55	38	15.5	84.5	0.5	0.1
Moulin SL						
12/09/2002	0.54	35	13.8	86.2	0.5	0.1
Moulin SL						
06/07/2006a	0.53	21	6.0	94.0	0.5	<0.1
Moulin SL						
06/07/2006b	0.62	45	19.4	80.6	0.5	0.1
Moulin SL						
12/07/2006	0.54	19	4.9	95.1	0.5	<0.1
Moulin SL						
08/09/2006a	0.54	24	7.6	92.4	0.5	<0.1
Moulin SL						
08/09/2006b	0.54	20	5.4	94.6	0.5	<0.1
Moulin SL						
15/09/2006a	0.53	23	7.1	92.9	0.5	<0.1
Moulin SL						
15/09/2006b	0.53	21	6.0	94.0	0.5	<0.1
Moulin SL						
24/09/2006	0.52	19	4.9	95.1	0.5	<0.1
Moulin SL						
20/10/2006a	0.53	45	19.4	80.6	0.4	0.1
Moulin SL						
20/10/2006b	0.58	52	23.3	76.7	0.4	0.1
Moulin SL						
07/12/2006	0.51	22	6.5	93.5	0.5	<0.1
Moulin SL						
05/06/2007a	0.58	17	3.7	96.3	0.6	<0.1
Moulin SL						
05/06/2007b	0.52	40	16.6	83.4	0.4	0.1
Moulin SL						
23/11/2007	0.53	21	6.0	94.0	0.5	<0.1
Moulin SL						
12/01/2008a	0.58	33	12.7	87.3	0.5	0.1
Moulin SL						
12/01/2008b	0.50	26	8.8	91.2	0.5	<0.1
Average	0.54	32	12.1	87.9	0.5	0.1

table 3

year	Laval		Moulin	
	sediment yield (t km ⁻² yr ⁻¹)	FOC yield (t km ⁻² yr ⁻¹)	sediment yield (t km ⁻² yr ⁻¹)	FOC yield (t km ⁻² yr ⁻¹)
1985	6188	31		
1986	10812	54		
1987	11288	56		
1988	7004	35	3564	18
1989	4352	22	1350	7
1990	12308	62	6534	33
1991	9180	46	5346	27
1992	21148	106	9990	50
1993	11968	60	6156	31
1994	18360	92	9396	47
1995	9452	47	4374	22
1996	17884	89	8424	42
1997	8704	44	4536	23
1998	7140	36	4590	23
1999	9996	50	4590	23
2000	13668	68	5562	28
2001	8772	44	6588	33
2002	12716	64	6642	33
2003	15300	77	5130	26
2004	17952	90	9180	46
2005	13328	67	5670	28
Average	11787	59	5979	30

table 4

catchment	dissolved load yield (Cras, 2005) (t km ⁻² yr ⁻¹)	[Ca ²⁺] (Cras, 2005) (mmol l ⁻¹)	average TDS (Cras, 2005) (mmol l ⁻¹)
Laval	340	2.5	13.4
Moulin	570	2.4	11.7

fig1

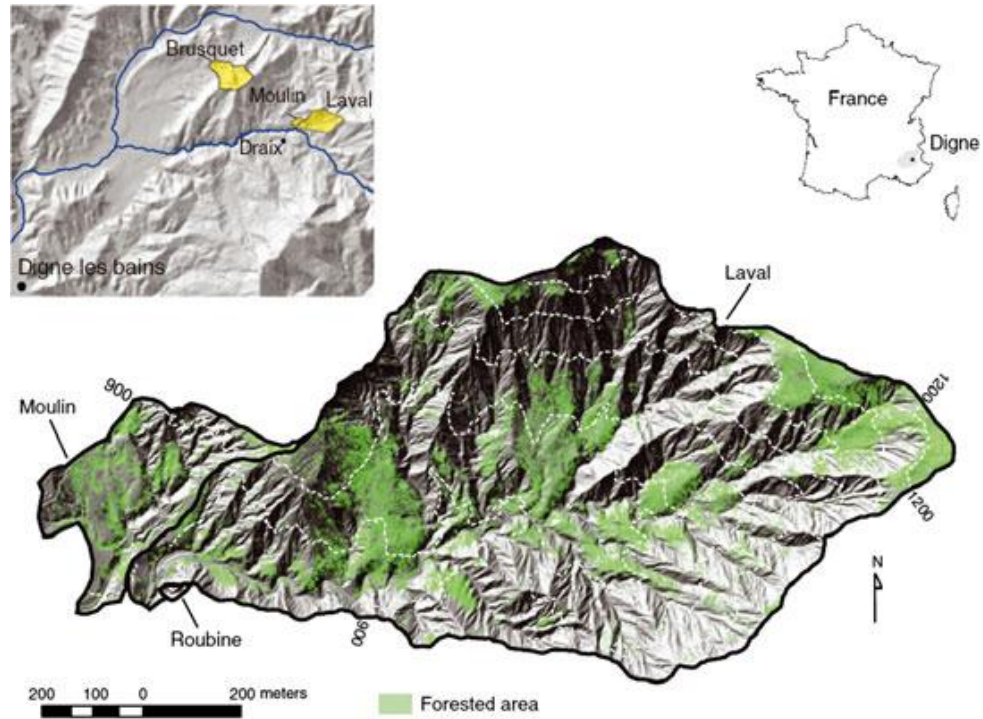


Fig2

